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Sorption Properties of Aerogel in Liquid Nitrogen

Wesley L. Johnson*
Auburn University, Auburn, AL, 36849

Aerogel products are now available as insulation materials of the future. The Cryogenics Test Laboratory at the NASA Kennedy Space Center is developing aerogel-based thermal insulation systems for space launch applications. Aerogel beads (Cabot Nanogel®) and aerogel blankets (Aspen Aerogels Spaceloft®) have outstanding ambient pressure thermal performance that makes them useful for applications where sealing is not possible. Aerogel beads are open-celled silicone dioxide and have tiny pores that run throughout the body of the bead. It has also recently been discovered that aerogel beads can be used as a filtering device for aqueous compounds at room temperature. With their hydrophobic covering, the beads absorb any non-polar substance and they can be chemically altered to absorb hot gases. The combination of the absorption and cryogenic insulating properties of aerogel beads have never been studied together. For future cryogenic insulation applications, it is crucial to know how the beads react while immersed in cryogenic liquids, most notably liquid nitrogen. Aerogel beads in loose-fill situation and aerogel blankets with composite fiber structure have been tested for absorption properties. Depending on the type of aerogel used and the preparation, preliminary results show the material can absorb up to seven times its own weight of liquid nitrogen, corresponding to a volumetric ratio of 0.70 (unit volume nitrogen per unit volume aerogel). These tests allow for an estimate on how much insulation is needed in certain situations. The theory behind the different processes of sorption is necessary for a better understanding of the preparation of the beads before they are used in an insulation system.

I. Introduction

OFTEN around liquid hydrogen and liquid oxygen tanks, there are areas where previously insulation could not be applied. Instead nitrogen and helium gas purges are run to eliminate the liquefaction of air and therefore the oxygen that is in the air. Liquefied oxygen poses a high explosion and flammability hazard as it will easily oxidize any fuel and cause a large explosion if force is then applied to the mixture. Gaseous purges are used frequently when the geometry of a cryogenic surface is too complex for spray on foam and the container can not be vacuum insulated. Often this occurs where the container structure cannot be designed to withstand a vacuum. Usually either nitrogen or helium is used as a purge gas. Helium is by far the more expensive gas of the two. However, when the cryogenic surface gets cooler than 77 K (the liquefaction point of nitrogen), helium is the only gas that will prevent the build up of liquid on the surface. If a loose-fill insulation system can be designed so that a nitrogen purge can be run into areas where the surfaces are protected by some insulation that does not require adherence to the surface to prevent liquefaction of the nitrogen gas in the free volume, then much money can be saved and gaseous helium can be conserved. For example, cryogenic propellant tanks are often a part of the structure of a fluids system. This makes it logistically and cost effectively impossible to maintain a vacuum around the system. However, air cannot be allowed around the tanks because of the dangers involved with the liquefaction of oxygen. Such systems are under research and development by the Cryogenics Test Laboratory at the NASA Kennedy Space Center and more knowledge of the liquid nitrogen sorption capacity of the aerogel is needed.¹

It has been noted at the Cryogenics Test Laboratory that aerogel beads (Cabot Nanogel®), when poured into liquid nitrogen (LN2), cause the LN2 to disappear. However, there is not enough gaseous nitrogen boil-off (off-gassing; substance that is turned into a gas due to the change of state from either liquid or solid form) for all the nitrogen to have been evaporated. Upon further examination, it has been noticed that upon placing the aerogel in one's hand, that the beads immediately begin off-gassing at a higher rate. If a small amount of beads are placed into a large, sealed plastic bag and placed in a hand or on a metal table, the bag quickly expands and will explode if the pressure is not relieved. Upon resealing the bag, it once again expands. This process can be repeated multiple times depending on the amount of aerogel placed in the bag and the process of relieving the large quantities of gas. Aerogel is also used as an adsorbent in water purification as well as toxic metal clean up. In these situations, it is treated to absorb certain chemicals and remove them from a situation where they might pose a threat to humans.^{2,3} The author has experienced that when aerogel was let to circulate through a large closed circuit wind tunnel, the

*Student, Aerospace Engineering Department, 211 Aerospace Engineering Building, Student Member

aerogel turned yellow as it absorbed all the oil and grease that was on the floor and walls of the wind tunnel. From these facts it is reasonable to conclude that the aerogel is likely absorbing the nitrogen into its many pores.

A. AEROGEL MATERIAL PROPERTIES

Aerogel is open-celled silicone dioxide that has tiny pores that run throughout the body of the bead. The individual beads allow aerogel to be used in many different situations. Unlike spray on foam, it can be moved after initial installation without hurting its insulation properties or structural integrity. Other forms of high performance insulations like perlite and multi-layered insulation (MLI) need to be placed in high vacuum to be effective. Aerogel on the other hand, outperforms these other forms of insulation at ambient pressures (1 atmosphere). The bead density of aerogel is 140 kg/m^3 (8.74 lb/ft^3); however due to its low packing density its bulk (installed) density is only 80 kg/m^3 (5.0 lb/ft^3). Because of its porous nature, aerogel has a measured surface area of $650 \text{ m}^2/\text{g}$ ($4.57 \cdot 10^8 \text{ in}^2/\text{lbm}$).⁴ The aerogel beads have a porosity of at least 90%, with an average pore diameter of 20 nm. The nominal diameter of the beads is 1 mm.⁴ Aspen's Spaceloft (aerogel blanket) material is basically aerogel formed within in a fiber matrix. The aerogel blanket is slightly denser (101 kg/m^3 , 6.3 lb/ft^3) than the beads. Considering the similar physical properties, their absorption properties are also expected to be similar, though the small differences from their structural differences may be noticeable.

B. CRYOPUMPING PHENOMENON

This high surface area of aerogel allows for large amounts of cryopumping. Cryopumping only occurs when a surface is cooled to a cryogenic temperature ($T < 150 \text{ K}$). The resulting temperature causes the gas around the surface to be condensed on to the surface in either the form of a liquid or a solid. In many instances this has been used to create high level vacuums and most research in the cryopumping field has been related to vacuum technology. Sorption is the overarching description of cryopumping. There are two methods of sorption, adsorption and absorption. Adsorption is when the particles are initially attracted to the surface of a material by either physical or chemical means. Absorption in the studied cases can be reduced to solid diffusion.⁵

There are several different types of cryopumping: cryosorption, cryocondensation, and cryotrapping. Cryotrapping is when a substance (usually water) within a system is rapidly frozen and traps within it other gasses. Ice crystals have a surface area of roughly $600 \text{ m}^2/\text{g}$, which is approximately the same as aerogel ($650 \text{ m}^2/\text{g}$).^{4,5} However cryotrapping also limits the pore volume because it occupies the volume that could be filled with absorbed gas. Cryocondensation is where gas molecules are collected by other molecules of the same material that are already coating a cold surface. Cryosorption, the physical adsorption of the molecules, is when the molecules stick to the surface of the aerogel.⁵ All of these combine under one general fact, when a surface gets cold, vapors tend to condense on it. It seems as though with cryotrapping eliminated, that cryosorption is the main initial driving force for adsorbing the liquid with cryocondensation helping to catch any gasses that may try to escape. This is the theory used in the many different cryogenic vacuum pumps used today and for the same reason aerogel, with its high surface area per unit weight, is a good adsorbent.

When the gasses inside the pores of the aerogel are chilled, the pressure drops, causing nitrogen to be attracted to the surface of the aerogel. After the initial surface attraction, the nitrogen is then absorbed into the pores of the aerogel where it is thermally isolated from its surroundings by the low thermal conductivity of the aerogel.

II. Experimental Procedures

There were two different methods of tests carried out. The first test was intended to measure the volumetric ratio of LN2 absorbed in the loose-fill aerogel. The second test was a modified version of the first that measured the weight ratio in both loose-fill beads and the aerogel blankets.

To begin the first series of testing, a vacuum jacketed bowl was marked at 100, 200, and 300 mL using water as the standard fill. The water was then removed, the bowl completely cleaned while the fill marks remained. The bowl was then filled with LN2 to a point well above the desired fill level. This allowed the bowl to be quenched by the LN2 with still more liquid than desired for a test. The LN2 was then allowed to sit and evaporate until the desired fill level was reached. The evaporation rate of the LN2 using this method was very slow and it often took several hours and cycles to reach the exact desired level. During this period, a specific amount of aerogel was poured into the same measuring standard as the water had been previously (after a thorough drying). When the LN2 reached the desired level, the aerogel was slowly poured into the bowl to try and maintain the nitrogen as calm as possible. Once the aerogel had all been poured into the bowl, a wooden tongue depressor (low heat leak) was used to push aside a path to the bottom of the bowl. Usually, more aerogel was used (on a volume basis) than LN2, so there was dry

aerogel on the top. This aerogel was then pushed down to fill the path and absorb any nitrogen that had not been absorbed during the initial pour. This was repeated until there was no more nitrogen in the bottom of the dish. If not all nitrogen was absorbed in a reasonable amount of time, it was assumed that there was not enough aerogel present. Due to the visual difference between cold and relatively warm aerogel, if all nitrogen was absorbed and there was still a decent amount of warm aerogel, it was assumed that there was a greater amount of aerogel present than needed.

The second test method was found to be much easier and more accurate. First an unmeasured amount of LN2 was poured into the vacuum jacketed bowl. Then a sample of aerogel blanket (or aerogel beads in a confined volume also called a tea bag in test results) was weighed on a digital scale. The sample was then placed in the bowl of LN2 and allowed to absorb all of the nitrogen it could hold. When the sample was removed, a quick visual check was done to make sure that the sample appeared fully saturated with LN2 before it was quickly placed on the scale and the initial reading was recorded. By rapidly proceeding through the last two steps, it was assumed that very little nitrogen escaped and little air condensed on the sample before the initial reading was taken. This test was then repeated with the test specimens treated beforehand by placing them in a vacuum chamber overnight and then filling the chamber with gaseous nitrogen to eliminate the cryotrapping phenomenon with respect to water vapor.

III. Experimental Results and Observations

Initial testing of the beads was run at various liquid levels (100, 200, and 300 mL). These studied the initial ratio (at 100 mL) and then scaling from there. In total, four tests were run at 100 mL, six tests were run at 200 mL, two tests at 300 mL, and one test at 615 mL of liquid. These tests indicated a volumetric ratio of approximately 0.75 (mL LN2 per mL aerogel). The average ratio for tests was 0.77 mL/mL with a mathematical standard deviation of 0.005 mL/mL (see Table 1). However, these results do not take into account the cooling of the aerogel beads or the human error associated with this experiment. Using the ratio of the densities of liquid nitrogen and aerogel, a 0.77 mL/mL volumetric ratio is equivalent to a 7.8 unit mass LN2 absorbed per unit mass aerogel.

Aerogel Absorption Testing						
Test Type: Volumetric ratio						
Date	Test No.	Initial LN2 Level (mL)	Amount of beads (mL)	Ratio	MassRatio	
11/1/2005	VR1	615	840	0.732	7.413	
11/1/2005	VR2	100	165	0.606	6.136	
11/2/2005	VR3	100	140	0.714	7.232	
11/2/2005	VR4	100	130	0.769	7.788	
11/4/2005	VR5	100	120	0.833	8.438	
11/16/2005	VR6	200	260	0.769	7.788	
11/16/2005	VR7	200	260	0.769	7.788	
11/29/2005	VR8	200	265	0.755	7.642	
11/29/2005	VR9	200	265	0.755	7.642	
12/1/2005	VR10	200	262.5	0.762	7.714	
12/6/2005	VR11	300	390	0.769	7.788	
12/7/2005	VR12	200	260	0.769	7.788	
12/7/2005	VR13	300	390	0.769	7.788	
12/15/2005	VR14	100	130	0.769	7.788	
12/15/2005	VR15	100	130	0.769	7.788	

Table 1. Test results from the first method with no treatment. Results were measured in volumetric ratios which were then correlated to mass ratios using density.

The second series of tests yielded higher quality results. Using a contained solid system, there was no longer any worry about cooling the beads. The only LN2 that mattered was that which was absorbed by the aerogel. Three different sizes of aerogel blanket were used, two weighing about three grams, and the third about a gram. The three different sizes were each run at least three times for a total of ten tests. The different samples of aerogel blanket were labeled Large #1, Large #2, Small, and Square to be able to distinguish between samples. Also a colander (called tea bag in test results) was tested containing aerogel beads. The colander was held so that all of the aerogel

was submerged in liquid nitrogen for several minutes, when they were removed, liquid nitrogen was dripping from them. The liquid stopped dripping by the time the scale was reached. Tests were also run with an empty colander to make sure the strainer didn't absorb any liquid. The results from all of the specimens were very similar. The average mass ratio for the successful tests was 6.2 units mass LN2 absorbed per unit mass aerogel. The standard deviation was 0.035 mass/mass.

Aerogel Absorption Testing			Warm Tea Bag		15.5		
Test Type: Weight gain			Cold Tea Bag		16		
Date	Test No.	Sample	Initial Weight (g)	Final Weight (g)	Weight LN2 (g)	Ratio (LN2/aerogel)	Volume Ratio
12/6/2005	WG1	Small	1.31	9.70	8.39	6.42	0.63
12/7/2005	WG2	Large #1	3.35	24.10	20.75	6.20	0.61
12/7/2005	WG3	Large #1	3.34	24.30	20.96	6.28	0.62
12/7/2005	WG4	Large #1	3.29	23.00	19.71	5.98	0.59
12/7/2005	WG5	Large #1	3.26	23.50	20.24	6.21	0.61
12/7/2005	WG6	Large #2	3.15	24.00	20.85	6.61	0.65
12/9/2005	WG7	Tea bag	4.40		27.20	6.18	0.61
12/9/2005	WG8	Small	0.99	7.20	6.21	6.26	0.62
12/14/2005	WG9	Tea bag	4.49	32.40	27.91	6.21	0.61
12/14/2005	WG10	Tea bag	4.57	33.00	28.43	6.22	0.61
12/14/2005	WG11	Tea bag	4.60	33.43	28.83	6.27	0.62
12/14/2005	WG12	Large #2	3.11	24.80	21.69	6.98	0.69
12/15/2005	WG13	Large #2	3.102	22.71	19.61	6.32	0.62
12/15/2005	WG14	Small	0.832	6.098	5.27	6.33	0.62

Table 2. Results from second method with no special preparation. Results were measured in mass ratios which were then correlated to volumetric ratios using density.

In an effort to eliminate any trapped water vapor from within the beads that might cause cryotrapping, the samples were then put in a vacuum chamber overnight with a mechanical vacuum pump that quickly had the residual gas pressure below 30 inches of mercury of vacuum. After sitting with several hours of heating at 100 °F the next day, the vacuum pump was stopped and the chamber was filled with gaseous nitrogen. The samples were then removed from the purge, weighed, and placed in the bowl of LN2. After sufficient time, the samples were removed and weighed. The percentage weight gain showed a marked increase, this increase differed between the aerogel blanket and the aerogel loose fill (in the sieve). The average weight gain ration was 7.05 units mass LN2 absorbed per unit mass aerogel for the used aerogel blanket ("Large #1" and "Large #2") and 6.5 units mass LN2 absorbed per unit mass aerogel for the loose fill in the sieve. These were obtained using the same procedure as was used before the purge. As noted in Table 3, the piece of aerogel blanket called "Square" was previously unused; where as the other pieces were slightly worn with the exception of "Small" which was well worn. The unused "Square" showed a noticeably higher level of sorption.

Aerogel Absorption Testing			Warm Tea Bag		15.5		
Test Type: Nitrogen Purge + Vacuum			Cold Tea Bag		16		
Date	Test No.	Sample	Initial Weight (g)	Final Weight (g)	Weight LN2 (g)	Ratio (LN2/aerogel)	Volume Ratio
12/20/2005	VN1	Large #1	3.19	25.16	21.97	6.89	0.68
12/20/2005	VN2	Large #2	2.98	24.00	21.02	7.05	0.70
12/20/2005	VN3	Small	0.77	6.36	5.59	7.26	0.72
12/20/2005	VN4	Square	3.20	28.40	25.20	7.88	0.78
12/20/2005	VN5	Large #1	3.21	26.37	23.16	7.21	0.71
12/20/2005	VN6	Large #2	3.05	24.10	21.05	6.90	0.68
12/20/2005	VN7	Small	0.77	6.65	5.88	7.64	0.75
12/20/2005	VN8	Square	3.05	28.00	24.95	8.18	0.81
12/20/2005	VN9	Tea Bag	4.48	33.71	29.23	6.52	0.64
12/20/2005	VN10	Tea Bag	4.47	33.31	28.84	6.45	0.64
12/21/2005	VN11	Large #1	3.20	25.80	22.60	7.06	0.70
12/21/2005	VN12	Large #2	2.93	23.50	20.57	7.02	0.69
12/21/2005	VN13	Small	0.76	6.80	6.04	7.95	0.78
12/21/2005	VN14	Square	2.94	26.10	23.16	7.88	0.78
12/21/2005	VN15	Tea Bag	4.29	32.00	27.71	6.46	0.64
12/21/2005	VN16	Large #1	3.15	26.34	23.19	7.36	0.73
12/21/2005	VN17	Large #2	2.92	23.50	20.58	7.05	0.70
12/21/2005	VN18	Small	0.75	7.10	6.35	8.47	0.84
12/21/2005	VN19	Square	2.87	26.80	23.93	8.34	0.82
12/21/2005	VN20	Tea Bag	4.13	30.80	26.67	6.46	0.64
	Large #1	Large #2	Square	Tea Bag	Small		
average	7.13	7.01		8.07	6.47	7.83	
st. dev	0.20	0.07		0.23	0.03	0.51	
average all	7.30						
st. dev. All	0.638565						
Square was virgin before these tests							

Table 3. Test results from Vacuum and nitrogen purge preparation of the aerogel beads using second method. Results were measured in mass ratios which were then correlated to volumetric ratios using density.

Several interesting changes were noticed after the aerogel was placed in the nitrogen purge. First, in the pre-purge (original) tests, the aerogel blanket would immediately cause a large gas plume to be emitted from the LN2 bowl due to liquid being gasified. However, in the GN2 based tests, the gas plume was much smaller. This indicates a lower specific heat due to the removal of water vapor and oxygen (which liquefies before nitrogen) that is in the air. Also, in the original tests, the specimen would initially float, but then after a short while it would begin to sink, however in the GN2 purged tests, the aerogel blanket never reached the point of sinking. Even though it was left in the bowl for much longer than in the original on several tests to see if it would sink, it never began to sink. This indicates a change of density due to the vacuum and nitrogen purge. It was also noticed during both cool downs that gas bubbles were constantly rising to the surface of the nitrogen, these bubbles slowed down at a time after insertion, but never completely stopped. The most obvious observation is that the cryosorption capacity of the aerogel is dependant on the presence of water vapor present to crystallize within the bead structure. This dependence seems to be more pronounced in the aerogel blanket than the loose fill beads. The third series of tests showed the aerogel beads had a clear dependence on cryotrapping and the presence of water vapor in its pores.

A. Experimental Error

The first method of testing yielded considerable error. The specific heat for aerogel is unknown and so the amount of LN2 boil off due to the cooling of aerogel could be significant. Also there were several uncontrolled human elements, such as how the mixing process was done and how fast the beads were poured into the liquid nitrogen. In addition, the amount of liquid nitrogen in the bowl was only as accurate as the eye could see. The lines were not perfectly drawn on the bowl as water ruins permanent markers, so to preserve the markers often the marks were slightly off. The final result was a human judgment on whether the stirring was appropriate or not. This brought in error of at least twenty-five percent for the overall test based on the results obtained from the second series of testing.

Most of these sources of error were eliminated or minimized using the second test method. A source of error for the second test were water vapor condensing out of the air onto the test article while it was being moved from the LN2 bath to the scale for measurement. This was measured during an empty (no aerogel) run with the tea bag and factored into all the results. The accuracy of the scale plays only a minimal factor because the accuracy of the scale is to the nearest milligram; however the post LN2 baths were only recorded to the nearest tenth of a gram with a hundredth recorded on rare occasion. The largest source of error still occurred when measuring the sample full of liquid, the first number seen was recorded and as the liquid was always leaving the system in the form of gas, the weight would quickly decrease as it sat on the scale; this meant that the tester had to be quick in looking for the initial weight. However, the transfer from the LN2 bath to the scale was a short duration in comparison to the time the beads will hold the nitrogen (over an hour) that it was assumed that only a very little was lost in comparison to the whole amount. Though it would be very hard to put an exact error on this method, it is estimated to be less than five percent; a reading error of approximately 0.35 grams would cause a five percent error at the reported result.

IV. Conclusion

The application of aerogel in either loose-fill or blanket type configurations can allow for much reduced purge system requirements for cryogenic structures. Without any preparation to the aerogel, the sorption ratio was approximately 6.2 units mass LN2 absorbed per unit mass aerogel. When the aerogel was given a vacuum and nitrogen gas back fill, the sorption mass ratios increased to 6.5 units mass per unit mass aerogel for the beads and 7.05 for the blankets. Initial testing indicated that the sorption is affected by the presence of water vapor in the air. Further testing should be conducted to determine if the sorption is a function of humidity or amount of water vapor in the air. This will determine the dependence on cryotrapping and the initial gas in the aerogel. Also, through the testing, it was noticed that new aerogel blankets tend to absorb more nitrogen than a used one. Overall, the aerogel blankets had a larger fluctuation of sorption capacity than did the beads. Through further research, different types of preparation should be studied in an attempt to determine what type of preparation might be most effective for a certain application. The continuation of this research will allow for the optimization of insulation systems, to ensure the sorption capacity of the insulation will suffice for the liquefaction of the gas.

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[†] Principle Investigator, Cryogenics Test Laboratory, Mail Code: KT-E, Kennedy Space Center, FL 32899